EFED

RED CHAPTER
For
Diclofop Methyl

March 22, 2000

Revised July 26, 2000

I RED Summary for Diclofop Methyl

Diclofop methyl (also known as Hoelon® 3EC) is a herbicide, first registered in 1982, for controlling a broad spectrum of annual grassy weeds in wheat and barley. Local need authorization has also been issued by 11 States for use of this chemical on Turf (Golf courses) to control goosegrass. It is not registered for any residential or non-agricultural uses. Present tolerances for the combined residues of diclofop methyl and its degradates has been established for wheat and barley (grain, straw) at 0.1 milligram/kilograms, or parts per million (ppm).

Diclofop methyl poses a potential risk of reproductive toxicity to mammals. Diclofop methyl is moderately toxic to mammals on an acute basis and also poses a minor acute risk to mammals. This herbicide is practically nontoxic to birds on an acute basis and therefore poses minimal acute risk to birds. This chemical generally poses low acute and chronic toxicity to fish and aquatic invertebrates, resulting in a very low risk to fish and aquatic invertebrates from exposure to the parent compound. Diclofop methyl has very low solubility (0.8 mg/l at pH 7, 25 ^{o}C). Under alkaline conditions, diclofop methyl rapidly hydrolyzes into diclofop acid, which is a polar compound and has relatively higher solubility (23 mg/l at pH 7, 20 ^{o}C) in water. However, the parent compound is immobile and the acid degradate has very low to intermediate mobility depending upon its environment. The maximum annual use rate for this chemical is 1.0 lb a.i./acre for all broadcast type applications. .For spot treatments, the maximum application rate is 1.0 fl oz per 1000 ft^2, or approximately 1.0 lb ai/A, the same as for broadcast applications. The maximum annual rate for spot treatment is 1.5 fl oz per 1000 ft^2, or 1.53 lb ai/A. The Studies with the rainbow trout and the oyster have shown that diclofop acid has much lower acute toxicity than the parent compound. Therefore, the Agency concludes that the risk of use of diclofop methyl according to the registered label will not pose a risk to aquatic fish or invertebrates. Runoff and spray drift from diclofop methyl poses a high risk to nontarget grasses and sedges and it is also assumed to pose high risk for nontarget aquatic plants since no toxicity data have been provided on these species.

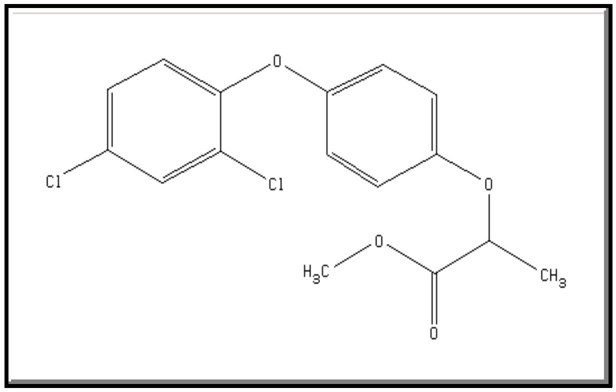
To monitor the environmental fate and transport of Diclofop methyl and its free acid metabolite in soil, soil water, and groundwater a small scale prospective ground water (PGW) study was undertaken in Wadena County, Minnesota. Detail findings from this study are furnished under Appendix C. Based upon the modeling, monitoring, and the PGW study, diclofop methyl is not expected to reach either ground water or surface water in significant quantities. It is not persistent in soil under aerobic conditions and has very low persistence in anaerobic soil or water. The residues that do reach surface water will likely be rapidly degraded by microbial metabolism. The results of the PGW study have indicated that either Diclofop Methyl or its acid Degradate did not migrate even in trace quantities to the groundwater during the two- plus- year study in a worst case scenario application. This field study site was carefully selected by EPA's expert team from EFED who considered various site selection criteria. The study was also carried out in an EPA/OPP approved protocol. The tracers used in the study did reach groundwater in 28 days indicating normal recharge of the aquifer.

All of the data requirement have been fulfilled except avian reproduction study (guideline 71-4), aquatic plant growth study (guideline 123-2), and bioaccumulation in fish study (guideline

165-4) at the present time. However, there is sufficient information available from the acceptable, supplemental and unacceptable studies to make a preliminary qualitative assessment of the fate and effects of diclofop methyl in the environment at the present time. Table A under Appendices, at the end, provides the summary status of all the environmental fate and ecotoxicology data requirements.

II Introduction (Diclofop Methyl)

Common Name: Diclofop methyl
Chemical Name: 2-[4-(2,4-dichlorophenoxy)-phenoxy]-propanoate
Chemical Structure:



Formulations: Emulsifiable concentrate (Active ingredient 34.7%, Inert ingredients 65.3% - equivalent to 3.0 lbs. a.i./gallon)

Physical/Chemical properties:

Molecular Formula:	$C_{16}H_{14}Cl_2O_4$	Solubility:	3.0 ppm @ 22°C
Molecular Weight:	341.2	Henry's Law Const.:	1.65E-10 atm $mole/m^3$
Vapor Pressure:	3.45×10^{-6} Torr @ 25°C	Log K_{ow}:	4.58 @ 25°C
		pKa:	3.1

The following information about the solubility of Diclofop Methyl and its acid degradate is also included from a stability study.

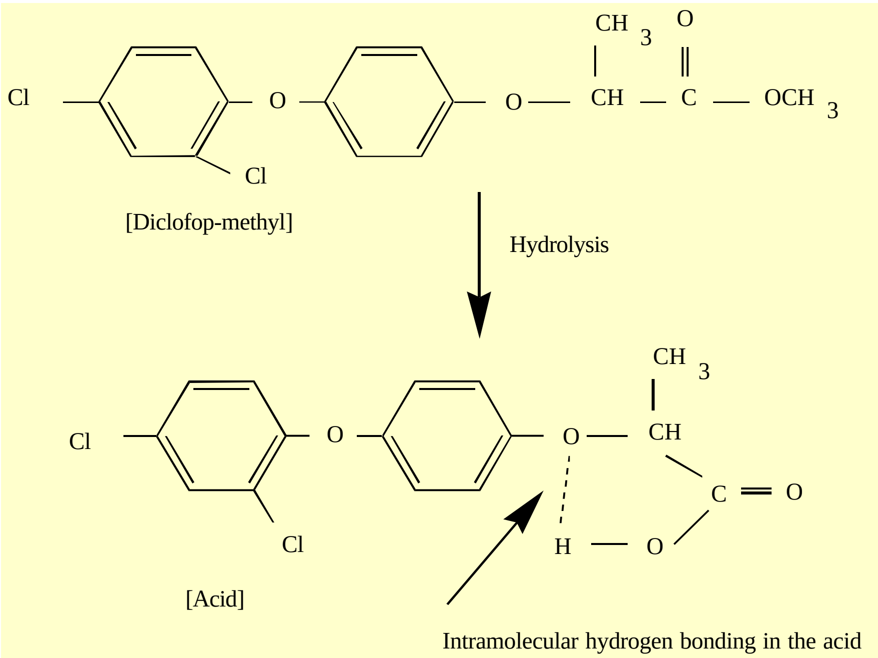
Diclofop methyl

Solubility in water: 0.743 mg/L (pH 7, 25 degrees C) (MRID 427964-01)
0.8 mg/L (pH 7, 20 degrees C) (MRID 408063-03)

Diclofop acid

Solubility in water: 23 mg/L (pH 7, 22 degrees C) (MRID 408063-02)
Dissociation constant: pKa=3.43 (MRID 424615-01)

Structure Showing Chemical Degradation of Parent to Diclofop Acid:



Mode of Action:

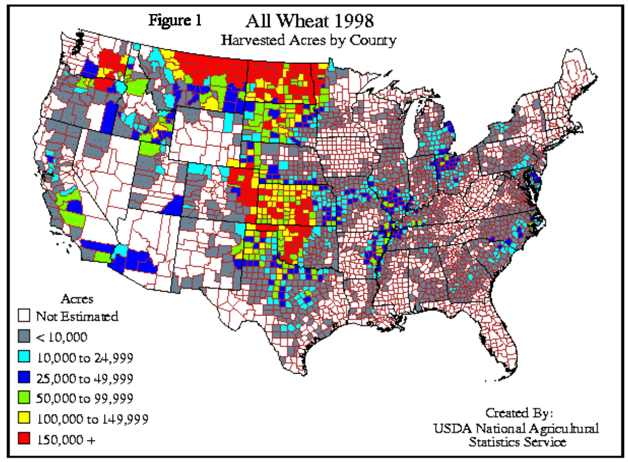
Selective systemic herbicide, also with contact action, absorbed primarily by the leaves, with some absorption by the roots in moist soil. Undergoes rapid transformation to diclofop, which is translocated within the plant. Destroys the cell membrane, prevents the translocation of assimilates to the roots, reduces the chlorophyl content, and inhibits the lipid/fatty acid by biosynthesis.

Use Characterization

Diclofop methyl is primarily used for controlling a broad spectrum of annual grassy weeds in wheat and barley. The major wheat and barley growing areas in U.S. are shown on Figure 1 and 2 respectively. Diclofop methyl usage map is shown on Figure 3.

Local need authorization has also been issued by 11 States (AL, AR, FL, GA, LA, MS, NC, OK, SC, TN, and TX) for use of this chemical on Turf (Golf courses) to control goosegrass. The method of application for this chemical is predominantly ground spray (90%+) and some aerial spray (5-10%).

It is not registered for any residential or non-agricultural uses. Present tolerances for the combined residues of diclofop methyl and its degradates has been established for wheat and barley (grain, straw) at 0.1 milligram/Kg or parts per million (ppm). This herbicide is used predominantly for a few specific annual grasses, such as wild oats, foxtail, ryegrass, and cheatgrass (downy brome). It is a foliar contact herbicide, which kills by reducing the plants ability to produce and utilize carbohydrates. It damages chloroplast membranes and thus prevents the plant from completing photosynthesis. The maximum annual use rate for this herbicide for turf use



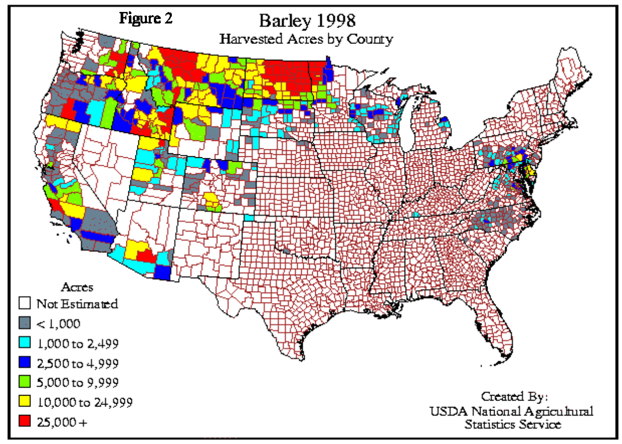
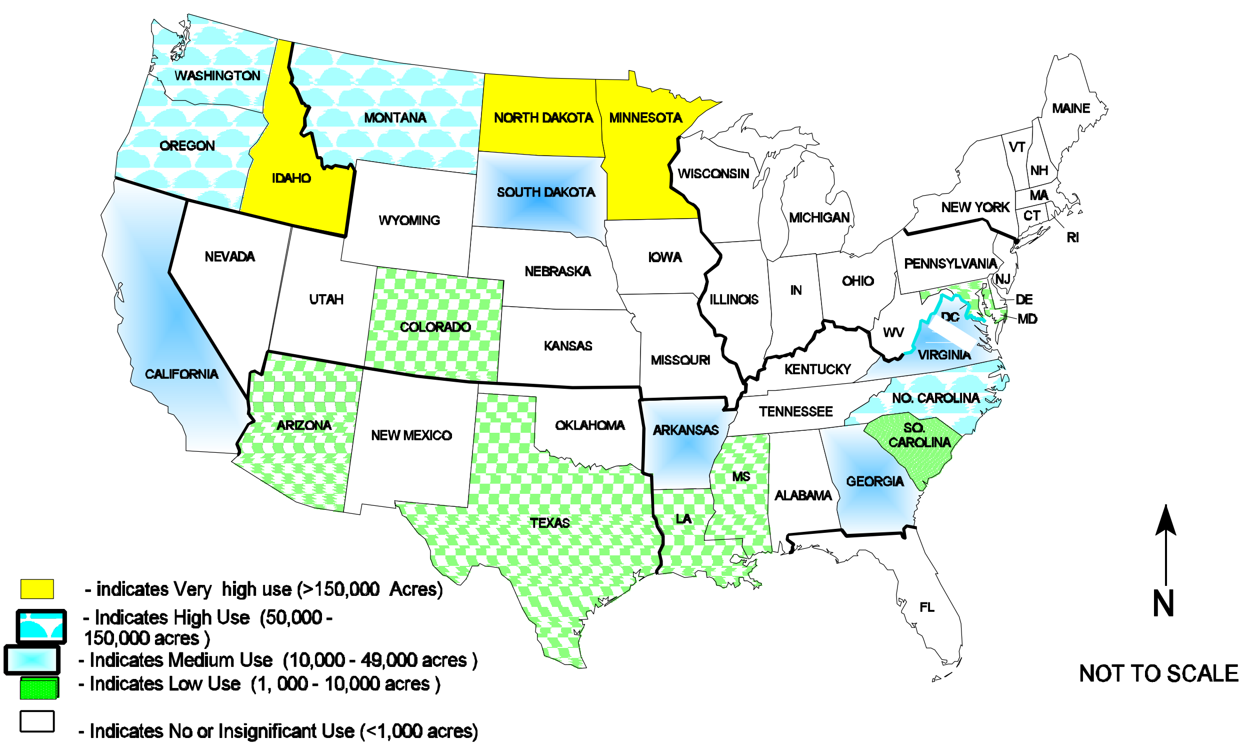


Figure 3 **Diclofop Methyl Usage in US**

Based upon 1995-97 Data



has been recently reduced by the registrant to 1 lb. active ingredient (a.i.)/acre for turf use in 11 States. This maximum annual rate of 1 lb. a.i./acre is commensurate with the small scale prospective groundwater study and the modeling inputs used to determine the migration and leachability of this herbicide to surface or ground water.

Approach to Ecological Risk Assessment

Terrestrial and aquatic risks were assessed for a single broadcast application of diclofop methyl at the rate of 1 lb ai/A. Risk to terrestrial organisms were also assessed for multiple spot-treatment applications. For spot treatments, the maximum application rate for spot treatments is 1.0 fl oz per 1000 ft^2, or approximately 1.0 lb ai/A, the same as for broadcast applications. The maximum per season or annual rate for spot treatment is 1.5 fl oz per 1000 ft^2, or 1.53 lb ai/A. Therefore, to assess the worst case use pattern, the assessment was based on a single application at 1.0 lb ai/A followed by a second application of 0.53 lb ai/A. The interapplication interval was assumed to be 7 days. Risk to aquatic organisms was not assessed for repeated spot-treatment applications because there were no risks identified for a single broadcast application. For aquatic exposure, the single broadcast application represents the worst-case use pattern because of significantly higher quantity of application and the area treated as compared to spot treatments.

The following example calculations show comparisons of spot treatments vs. regular broadcast application:

In **one acre of application -**
(Assuming 25 such spots in one acre)

$\boxed{\text{A}}$ ***spot treatments*** :

Total Maximum Area Treated $\approx$ 25 x 1000 ft^2 = 25,000 ft^2 = 25,000 ft^2 x 1 acre/43,560 ft^2
= 0.57 $\approx$ 0.6 Acres
With an annual Max. application rate of 1.53 lbs ai/acre for turf
Total volume/mass applied = 0.6 acre x 1.53 lbs ai/acre = ***0.92 lb***

$\boxed{\text{B}}$ ***Regular Broadcast Application:***

Total Maximum Area Treated $\approx$ 1 Acre
Annual Max. application rate = 1.0 lb ai/acre
Total volume/mass applied = 1.0 acre x 1.0 lb ai/acre = ***1.0 lb***

Thus, the impact of the regular broadcast application at 1.0 lb ai/acre would outweigh the impact of the spot treatments at a maximum annual application of 1.53 lb ai/acre in determining the exposure to aquatic ecosystems. The exposure to aquatic organisms was based on aquatic residues estimated using the PRZM/EXAMS model.

The risk of contaminating surface or ground water by diclofop methyl was evaluated by assessing the estimated environmental concentrations (EEC's) for both surface and ground water for parent diclofop methyl and the potential maximum population exposed through drinking water. Because of the lack of adequate monitoring data from across the country, the PRZM/EXAMS model was used to estimate the concentrations in surface water and the SCIGROW-2 model was used for estimating the concentrations of this chemical in ground water. A recently published water use data from the USGS, listing population served by surface and ground water, was used to estimate the potential maximum population exposed. Table 1 under Drinking Water Assessment, shows the diclofop methyl concentrations and potential maximum population exposed per 1995 water use data from USGS.

Some surface and ground water monitoring data have been found for diclofop methyl in the STORET data base for Minnesota and Idaho. Reported concentrations of diclofop methyl in the monitoring data were all below 0.1 ppb (μg/l).

III Integrated Environmental Risk Characterization for Diclofop Methyl

Diclofop methyl has very low solubility (0.8 mg/l at pH 7, 25 ºC). Under alkaline conditions, diclofop methyl rapidly hydrolyzes into diclofop acid, which is a polar compound and has relatively higher solubility (23 mg/l at pH 7, 20 ºC) in water. However, the parent compound is immobile and the acid degradate has very low to intermediate mobility depending upon its environment. The maximum annual use rate for this chemical is 1.0 lb a.i./acre for all broadcast type applications. .For spot treatments, the maximum application rate is 1.0 fl oz per 1000 ft^2, or approximately 1.0 lb ai/acre, the same as for broadcast applications. The environmental fate characteristics of diclofop methyl do not favor transport of this herbicide from the application sites to surface or ground water. In natural environment, the parent compound is rapidly transformed into the primary degradate, diclofop acid, through hydrolysis and/or microbial metabolism.

To monitor the environmental fate and transport of diclofop methyl and its free acid metabolite in soil, soil water, and groundwater a small scale prospective ground water (PGW) study was undertaken in Wadena County, Minnesota. Detail findings from this study are furnished under Appendix C. The PGW study have revealed that either Diclofop Methyl or its acid Degradate did not migrate even in trace quantities to the groundwater during this two-plus- year study. This field study site was carefully selected by EPA's expert team from EFED to represent a typically vulnerable area. The EFED scientists considered various selection criteria to pick this study site. The study was carried out in an EPA approved protocol as developed by EFED scientists. The tracers used in the study did reach groundwater in 28 days indicating normal recharge of the aquifer.

This lack of persistence and mobility, coupled with generally low acute and chronic toxicity to fish and aquatic invertebrates, result in a very low risk to fish and aquatic invertebrates from exposure to the parent compound. Under alkaline conditions, diclofop methyl rapidly hydrolyzes into diclofop acid, which has a relatively higher solubility in water compared to its parent. However, studies with the rainbow trout and the oyster have shown that diclofop acid has much lower acute toxicity than the parent compound. This lower toxicity is expected since diclofop acid is formed through hydrolysis of an ester group on the parent compound, which liberates a carboxyl group. This reaction, which makes the molecule more water soluble and susceptible to conjugation, is similar to the phase-I biotransformation reaction that are catalyzed by esterases in the liver of vertebrates to detoxicate esters contaminants (Klaassen et al., 1986). Diclofop acid is the only degradation product of diclofop methyl likely to be present in surface water in significant amounts. Therefore, the Agency concludes that the risk of use of diclofop methyl according to the registered label will not pose a risk to aquatic fish or invertebrates.

No toxicity data have been submitted to the Agency on the toxicity of diclofop methyl or diclofop acid to aquatic plants. Being an herbicide, diclofop methyl is expected to be toxic to aquatic plants. The parent compound could be toxic to aquatic plants even at the low concentrations that are expected to reach surface water. Additionally, the primary degradation product, diclofop acid, which could reach surface water in greater, could also be toxic to aquatic plants. Therefore, until data are available to conduct a risk assessment for aquatic plants, use of diclofop methyl should be assumed to pose high risk to aquatic plants. Furthermore, seedling emergence test show that soil contamination of diclofop methyl is highly toxic to emerging grass seedlings. Therefore, contamination of sediments by diclofop methyl would also be expected to pose a high risk to submerged and emerged aquatic grasses and sedges.

Use of diclofop methyl is generally expected to pose minimal risk to birds. Diclofop methyl is practically nontoxic to birds on an acute basis and is predicted to pose negligible acute risk to birds. Chronic risk is somewhat uncertain because the avian reproduction tests only evaluated to dietary concentrations 200 ppm ai, whereas peak terrestrial EEC's after an application of 1 lb ai/A are expected to be as high as 240 ppm on short vegetation. Since the highest dietary test concentration of 200 ppm caused no observable chronic effects, it is unlikely that significant chronic effects would be observed at the slightly higher concentration of 240 ppm. Furthermore, the registrant, Hoechst Celanese Corporation, has provided the Agency with summary data from field residue trials with wheat showing that residues of diclofop methyl and the acid degradation product were considerably less than 240 ppm and dissipated very rapidly from wheat foliage. In trials using application rates of 1.0 and 1.25 lb ai/A, foliage half-life values were estimated to be 0.42 and 1.25 days, respectively. Thus, assuming that these results are accurate and scientifically valid[1], foliage residues would be expected to be at levels exceeding the NOAEL level of 200 ppm for less than one day. Such a short exposure above the NOAEL would not likely cause any chronic effects in birds.

There is a very minor use of diclofop methyl on turf in which spot treatments may be made with repeated applications to up to 1.53 lb ai /A. In the risk assessment for this use, the maximum terrestrial EEC was estimated to be 331 ppm. This was based on an application of 1.0 lb ai/A followed by a second application of 0.53 lb ai/A 7 days later. The default value of 30 days was assumed for the half-life of diclofop methyl on foliage. The shorter half-lives of 0.42-1.25 days were not used because the studies that yielded these results have not been reviewed for acceptability by the EFED. The higher EEC for this use results in a greater margin of difference between the expected exposure level and the level shown to cause no observable chronic effects in the avian reproduction test. This, along with the opportunity for repeated applications, increases the possibilities of chronic effects to birds. However, spot treatments would entail treatment of relatively small areas. Birds would not likely feed exclusively in these treated areas, but would likely feed in untreated areas as well. Also, as stated above, the registrant has submitted summary data which indicates that the half-life on foliage is actually much less than the assumed 30 days. Altogether, the risk of chronic effects to birds from spot treatments of diclofop methyl on turf is uncertain but appears to be small.

Toxicity data indicate that diclofop methyl is more toxic to mammals than to birds, both on an acute and chronic basis. Despite being moderately toxic to mammals, the risk assessment indicated high acute risk only for repeated spot applications, and this conclusion is only for very small mammals feeding on food with the highest EEC's (short grass). As stated above, the half-life of residues on foliage has been shown to be very short. Therefore, any risk of acute toxicity to mammals would be short-lived because residues would rapidly drop below toxic levels. On the other hand, chronic risk to

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[1] This summary information was not used in the quantitative risk assessment because a detailed study report has not been submitted to and reviewed by the Agency. Nevertheless, EFED believes that it is important to consider these findings in the risk characterization discussion. We encourage the registrant to submit a detailed report to the Agency to allow the data to be formally reviewed and fully incorporated into the ecological risk assessment for diclofop-methyl.

mammals appears to be more serious. The maximum EEC for short grass following a single broadcast application at 1.0 lb ai/A (240 ppm) exceeds that level in mammal studies which have been shown to cause reproductive toxicity to rats. Risk quotients for chronic risk to mammals are as high as 8.0 for a single application at 1 lb ai/A and up to 11.0 for repeated spot applications. Thus, this screen indicates that use of diclofop methyl poses a chronic risk to mammals. This conclusion is uncertain because uncertainty of the persistence of diclofop methyl on foliage and the chronic toxicity of the major degradation product diclofop acid. The Agency could reassess the chronic risk to mammals if the registrant would provide data confirming the claimed rapid dissipation of residues from wheat foliage and data showing low chronic toxicity of diclofop acid to mammals.

Similar exposure levels of diclofop-methyl was found to induce adverse effects in rats in both a long-term 3 generation reproduction study (Acc. No. 097111) and a much shorter 15-week developmental study (Acc. No. 097108). In the developmental study, effects observed included resorption of fetuses and distention of the uterus. These results indicate that a short exposure to diclofop-methyl at a critical time of fetal development might be sufficient to adversely affect reproduction in mammals. Therefore, it is questionable whether rapid dissipation of foliar residues (if it does occur) would be enough to prevent reproductive impairment in wild mammals. Rapid dissipation of residues, however, would limit the extent of effects because there would be a relatively short window of time during which foliar residues would present a hazard to mammals.

Use of diclofop methyl poses minimal risk to bees because of the use pattern is not expected to result in significant exposure to bees and no significant toxicity to bees due to this herbicide has been reported in the literature.

Like most herbicides, diclofop methyl poses a risk to some terrestrial nontarget plants. The risk assessment for terrestrial plants indicated that risk is low from exposure of foliage to spray drift, but high from exposure of plant roots from a combination of runoff and spray drift. Risk quotients for soil exposure were 4.67 to 5.00 for plants in dry areas and 9.17 to 12.50 for semi-aquatic areas. Phytotoxicity data show that diclofop methyl is selectively toxic to monocotyledonous plants (i.e., grasses and sedges), but not very toxic to dicotyledonous plants (i.e., broadleaf plants). This is expected since the target plants of this herbicide are grass weeds. If risk quotients were based on toxicity to dicotyledonous plants, they would not exceed the level of concern. In conclusion, use of diclofop methyl poses a high risk to nontarget grasses and sedges from exposure in the soil, but the selectivity of the toxicity to grasses and the lack of risk from spray drift makes the overall risks from this herbicide less than that of many others.

A major uncertainty in the risk assessment for nontarget plants is the lack of phytotoxicity data for the primary degradation product, diclofop acid. Diclofop acid is relatively more persistent and mobile than is the parent, and is therefore more likely than the parent to contaminate soil in offsite habitats. The acid degradate of diclofop methyl may add to the overall risk to nontarget grasses and sedges from the use of this chemical.

<u>Endocrine Disruption</u>

EPA is required under the FFDCA, as amended by FQPA, to develop a screening program to determine whether certain substances (including all pesticide active ingredients) “may have an effect in humans that is similar to an effect produced by a naturally-occurring estrogen, or other such endocrine effect as the Administrator may designate.” Following the recommendations of its Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC), EPA determined that there was scientific basis for including , as part of the program, the androgen and thyroid hormone systems, in addition to the estrogen hormone system. EPA also adopted EDSTAC’s recommendations that the program include evaluation of potential effects in wildlife. For chemical pesticides, EPA will use FIFRA and, to the extent that effects in wildlife may help determine whether a substance may affect in humans, FFDCA authority to require wildlife evaluations. As the science develops and resources allow, screening of additional hormone systems may be added to the program. When the appropriate screening and testing protocols being considered under the Agency’s Endocrine Disruptor Screening Program have been developed, diclofop-methyl and/or diclofop acid may be subjected to additional screening and testing to better characterize effects related to endocrine disruption.

Diclofop methyl is suspected as being a possible endocrine disruptor because a recombinant yeast bioassay with trout estrogen receptors and a bioassay with trout hepatocyte cultures both indicate that it has estrogenic activity (Petit *et al*., 1997). Although mammalian toxicology studies indicate that the primary mode of action of diclofop methyl is toxicity to the liver and kidney, and does not provide evidence that diclofop-methyl causes effects related to disruption of the endocrine system. More research is required to determine if the estrogenic activity observed in the *in vitro* assays could give rise to any significant adverse effect in fish and wildlife at environmentally-relevant concentrations.

REFERENCE

Klaassen, C.D., M.O. Amdur, and J. Doull. 1986. Casarett and Doull’s Toxicology. 3rd Ed. Macmillan, New York. 974 pp.

Petit F., L.G. Goff, J.P. Cravedi, Y. Valotaire, and F. Pakdel. 1997. Two complementary bioassays for screening the estrogenic potency of xenobiotics: recombinant yeast for trout estrogen and trout hepatocyte cultures. J. Mol. Endocrinol. 19(3):321-335.

IV Environmental Fate Assessment

Environmental Fate Summary:

In field situations residue levels in the 0-6 inch soil layer dissipated with a half life of 19.3 days. Diclofop methyl was found to degrade rapidly in aerobic soil ($T_{1/2} \leq 1$ day) to its herbicidally active degradate, diclofop acid. The most likely routes of dissipation of the parent compound appears to be aerobic soil metabolism and possible transport with water. Hydrolysis and aqueous photolysis of parent are probably minor routes of dissipation in soil. Diclofop acid has relatively higher solubility (23 mg/l at pH 7, 20 ^{o}C) and low to intermediate mobility according to its physical/chemical characteristics (MRID# 408063-02). The major routes of dissipation of diclofop acid appears to be transport with water and aerobic soil metabolism. Further degradation of diclofop methyl residues results in a substantial amount of bound residues (25-42% of applied radioactivity in the aerobic soil metabolism study). A recent prospective groundwater study (PGW) was completed by the Registrant in Wadena County, Minnesota. Detail findings from this study are furnished under Appendix C. Study results up to 2 years after the initial application of diclofop methyl at 1 lb. active ingredient/acre show that no diclofop methyl or its acid degradate or any other residues leached to ground water. At the present maximum annual application rate of 1 lb. a.i/acre, the probability of contamination of ground or surface waters by diclofop methyl is considered to be very low.

Environmental Fate Assessment:

All of the fate data requirements have been fulfilled for diclofop methyl except the bioaccumulation in fish study (guideline 165-4) at the present time. However, there is sufficient information available from the acceptable, supplemental and unacceptable studies to make a preliminary qualitative assessment of the fate of diclofop methyl in the environment at the present time. Table A under Appendices, at the end, provides the summary status of all the environmental fate data requirements.

Diclofop methyl is not expected to reach ground or surface water under most conditions. Even if it reaches surface water, it is expected to degrade rapidly. If it would reach ground water, it could persist because of potentially low microbial activity.

Biodegradation is the predominant means of dissipation of diclofop-methyl dissipation; however, hydrolysis would also be a significant contributor to dissipation when the pH is low (<7). Parent diclofop methyl rapidly degrades in aerobic soil ($T_{1/2} \leq 1$ day) to its acid metabolite, diclofop acid. Diclofop methyl and its acid metabolite degraded with an estimated half life of 21 to 51.3 days in four aerobically incubated soils. Under anaerobic condition diclofop methyl degraded rapidly to diclofop acid. The diclofop-acid was extremely persistent under anaerobic conditions with a half life of greater than 60 days. Under almost all uses, the degradation is expected to be so rapid that diclofop methyl will not have time to move in soil. Its low solubility in water (0.8 mg/L at pH 7.0) also causes it to be immobile.

Diclofop-methyl is stable to hydrolysis at pH 5 with a reported half-life of 363 days.

Under alkaline conditions diclofop-methyl is unstable with a half-life of 12.5 hours at pH 9. In pH 7 buffer solution, diclofop-methyl is moderately stable with a half-life of approximately 32 days. Diclofop acid was the only degradate detected in any of the solutions, and it did not undergo any further hydrolytic degradation at any pH. The study was performed at 25°C. (MRID 41573309)

In another hydrolysis study (Acc. No. 244-465) performed at 21°C, it was demonstrated that diclofop methyl hydrolyzed rapidly at pH 9 with a half-life of 1.85 days, slowly at pH 7 with a half-life of 21.4 days, and at pH 5 the half-life was 2650 days. Diclofop acid was the only degradate detected in any of the solutions, and it did not undergo any further hydrolytic degradation at any pH.

Diclofop-methyl plus diclofop acid, the primary degradate, degraded with estimated half-lives of 21 to 51.3 days in four aerobically incubated soils. Parent diclofop-methyl was rapidly degraded to diclofop acid. Except for the sterilized soils, all the parent had been degraded by the 4th day of sampling to mainly diclofop acid. The concentration of the primary degradate reached it highest concentration at 1 or 2 days (77.7% of applied radioactivity, 1.17 ppm) and then decreased to an average 13.1% (0.2 ppm) of the applied radioactivity after 100 days of incubation. Diclofop acid degraded to diclofop phenol (4-(2,4-dichloro phenoxy)-phenol, but never was greater than 4% of applied radioactivity (0.06 ppm). Extractable residues accounted for 14-40% of the applied radioactivity by the termination of the study; while bound residues were 25-42% of applied radioactivity. (MRID 41573311).

Based on the mobility studies, EFED concludes that the mobility of parent diclofop methyl is not clear, in part due to the rapid conversion of parent to diclofop acid. However, in a study evaluating leaching of diclofop methyl through soil columns (Acc. No. 097120), the amount of parent found in the leachate of one soil (pH 7.0, organic matter 0.8%, sand 92.5%, silt 4.2% and clay 3.3%, CEC 3.0 meq/100g soil) was 17.81% of the applied radioactivity. Therefore, diclofop methyl may be mobile in sandy soils low in organic matter. Diclofop acid, the primary degradate, has the potential to be mobile, since K_d values from batch equilibrium studies were 0.7, 1.8 and 1.7 in silt loam, sand and silt loam soils, respectively. These adsorption coefficients indicate a low tendency to bind to soil.

The half-lives of the parent and diclofop acid in the two field dissipation studies were 2.6 and 3.5 and 26 and 28.4 days, respectively. The available data on field dissipation have not demonstrated significant leaching of residues of diclofop-methyl or its degradates. However, these data are extremely limited and no general conclusions about the leaching potential and likelihood of ground water contamination or surface runoff can be made at this time from the field dissipation data.

Because diclofop methyl metabolizes rapidly to diclofop acid after incorporation, and because the degradate is mobile to moderately mobile in soil, runoff to surface water of the degradate may follow a rainfall/irrigation event.

A small scale prospective ground water monitoring study for diclofop methyl was conducted in Wadena County, Minnesota. The study site was selected as representative of wheat production in cold climate where diclofop methyl usage was relatively high. Study results up to 2 years after the initial application of diclofop methyl at 1 lb. active ingredient/acre show that no diclofop methyl residues leached to ground water. Diclofop methyl was not detected in soil-pore water at concentrations above the Limit of Quantitation (1.0 ppb). The mean concentrations of diclofop methyl in the soil samples shortly after application on day after treatment (DAT) 0 from top 3 inches of soil in the test plot was 210 ppb. By the final sampling event on DAT 49, the mean concentration in top 3 inches of soil layer had decreased to 20 ppb. Diclofop residues in lower horizons were below the limit of quantitation (LOQ) except for a few detections of 10 ppb in the 6-12 inches interval at DAT 1. Residue levels in the 0-6 inch layer dissipated with a half-life of 19.3 days. Further details on the prospective groundwater (PGW) study is provided at the end of this report under Appendix C.

V Drinking Water Assessment

General Conclusions

Based upon the modeling, monitoring, and the small scale prospective ground water study, diclofop methyl is not expected to reach either ground water or surface water in significant quantities. It is not persistent in soil under aerobic conditions and has very low persistence in anaerobic soil or water. The residues that do reach surface water will likely be rapidly degraded by microbial metabolism. Diclofop methyl has very low solubility (0.8 mg/l at pH 7, 25 °C). Under alkaline conditions, diclofop methyl rapidly hydrolyzes into diclofop acid, which is a polar compound and has relatively higher solubility (23 mg/l at pH 7, 20 °C) in water. However, the parent compound is immobile and the acid degradate has very low to intermediate mobility depending upon its environment. The environmental fate characteristics of diclofop methyl do not favor transport of this herbicide from the application sites to surface or ground water.

This assessment contains estimated environmental concentrations (EEC's) for both surface and ground water for parent diclofop methyl and the potential maximum population exposed through drinking water. A recently published water use data from the USGS which lists population served by surface and ground water was used to estimate the potential maximum population exposed. Table 1 shows the diclofop methyl concentrations and potential maximum population exposed per 1995 water use data from USGS. This table contains data on all significant use areas as shown on Figure 3.

Some surface and ground water monitoring data have been found for diclofop methyl in the STORET data base for Minnesota and Idaho. Reported concentrations of diclofop methyl in the monitoring data were all below 0.1 ppb (μg/l).

Recommended Values for Dietary Risk Assessment

Table 2 presents the Tier 2 EEC's for **surface water** using PRZM/EXAMS. For surface water, the maximum upper 90th percentile concentration of 1.5 μg/l should be used for acute risk calculations. The 10-yr annual mean concentration of 0.1 μg/l should be used for chronic risk and cancer risk calculations. Table 3 presents the Tier 1 acute and chronic **ground water** concentrations using the SCI-GROW2 model.   For ground water, the predicted SCI-GROW2 concentration of 0.07 μg/l should be used for acute, chronic, and cancer risk assessment. The final report of the prospective ground water study indicated in the result of findings that at DAT 48 (Days After Treatment) bromide tracers were detected in the shallow ground water wells indicating recharge of aquifer, but no diclofop methyl or its acid metabolites were detected in the groundwater or soil water samples. EFED notes that the concentration in ground water is below the limit of quantitation (1 μg/l) of the prospective ground water study. Therefore, EFED cannot predict with certainty whether they will reach ground water. However, based on the environmental fate properties, and the prospective ground water study, diclofop methyl or its acid metabolite is not expected to reach ground water.

Table 1 DICLOFOP METHYL CONCENTRATIONS AND POTENTIAL MAXIMUM POPULATION EXPOSED
(Per 1995 Water Use data from USGS)

October 13, 1999

STATE	GROUND WATER		SURFACE WATER		Diclofop-Methyl Usage[3]	REMARKS
	Population Served	Predicted[1] Concentration (ppb)	Population Served	Predicted[2] Concentration (ppb)		
ARKANSAS	830,850	0.067	1,164,760	1.47	Medium	Used predicted concentration of 0.067 ppb for ground water by the SCI-GROW2 ground water model Surface water concentration is based on the PRZM-EXAMS model prediction Used 1995 data from USGS for the Population Served by surface and ground water.
ARIZONA	224,485	0.067	167,218	1.47	Low	Spring Wheat Usage
CALIFORNIA	13,012,920	0.067	17,453,370	1.47	Medium	Spring and Winter Wheat Usage
COLORADO	475,400	0.067	2,918,600	1.47	Low	Low usage on Spring Wheat
GEORGIA	1,676,770	0.067	4,222,760	1.47	Medium	Winter Wheat Usage
IDAHO	736,390	0.067	43,760	1.47	V. High	Very High usage on Winter Wheat, Barley and Spring Wheat
LOUISIANA	2,154,260	0.067	1,692,100	1.47	Low	Winter Wheat usage
MARYLAND	678,520	0.067	3,489,000	1.47	Low	Winter Wheat usage
MINNESOTA	2,405,220	0.067	936,080	1.47	Very High	Very High use on Spring Wheat and Barley

1. Concentration predicted by SCI-GROW2 groundwater model
2. Concentration predicted by PRZM/EXAMS model
3. Diclofop methyl usage (1995-97 data) in lb a.i(thousands): None - 0; Low - 0-10; Medium - 11-50; High - 51-150; Very High-150+

STATE	GROUND WATER		SURFACE WATER		Diclofop-Methyl Usage[3]	REMARKS
	Population Served	Predicted[1] Concentration (ppb)	Population Served	Predicted[2] Concentration (ppb)		
MISSISSIPPI	2,048,600	0.067	214,280	1.47	Low	Winter Wheat Usage
MONTANA	240,200	0.067	405,060	1.47	High	Barley, Winter Wheat, and Spring Wheat Usage.
NORTH CAROLINA	1,127,740	0.067	3,617,620	1.47	High	Usage on Barley and Winter Wheat
NORTH DAKOTA	213,170	0.067	276,310	1.47	Very High	Very high usage barley, Spring wheat, and Winter Wheat
OREGON	373,510	0.067	1,772,080	1.47	High	High usage on Spring and Winter Wheat
SOUTH CAROLINA	697,800	0.067	2,024,020	1.47	Medium	Barley and Winter Wheat usage
SOUTH DAKOTA	382,380	0.067	219,860	1.47	Medium	Barley and Spring Wheat usage
TEXAS	7,331,610	0.067	10,218,790	1.47	Low	Winter Wheat usage only
VIRGINIA	594,110	0.067	4,361,380	1.47	Medium	Winter Wheat and Barley usage
WASHINGTON	2,298,920	0.067	2,128,890	1.47	High	Winter Wheat, Spring Wheat, and Barley usage

1. Concentration predicted by SCI-GROW2 groundwater model
2. Concentration predicted by PRZM/EXAMS model
3. Diclofop methyl usage (1995-97 data) in lb a.i(thousands): None - 0; Low - 0-10; Medium - 11-50; High - 51-150; Very High-150+

All data requirements for the water assessment purpose are satisfied for diclofop methyl for the reregistration eligibility decision document. The input and output summary files for the PRZM/EXAMS are attached at the end under APPENDICES. The general surface water input variables are summarized in Table 4 below. Table 5 lists the SCI-GROW2 inputs for diclofop methyl.

Table 2. Tier 2 upper 90th percentile EEC's in Surface Water for Parent Diclofop-methyl using PRZM/EXAMS.[*]

Compound	Maximum (µg/l)	4 Day (µg/l)	21 Day (µg/l)	60 Day (µg/l)	1 in 10-Yr. Annual Mean[1] (µg/l)
Diclofop-methyl and metabolites	1.47	1.37	1.11	0.73	0.097

[1] - To be used for chronic and cancer risk calculations.

Table 3. Acute and Chronic Concentrations of Parent Diclofop methyl and Metabolites in Ground Water Using SCI-GROW.[*]

Compound	Acute (µg ·L^{-1})	Chronic (µg ·L^{1})	Cancer (µg ·L^{-1})
Parent Diclofop-methyl and metabolites	0.067	0.067	0.067

[*] EFED notes that the predicted concentration in ground water is below the limit of quantitation (1 μg/l) of the prospective ground water study conducted for this chemical. Therefore, EFED cannot predict with certainty whether they will reach ground water. However, based on the environmental fate properties, and the PGW study conducted for over two years in Wadena County, MN, diclofop methyl is not expected to reach ground water.

Surface Water Inputs

The input summary file for the PRZM/EXAMS is attached at the end of this document. However, Table 4 below lists the values used for common surface water input variables.

Table 4. General Surface Water Input Variables for Parent Diclofop methyl.

MODEL INPUT VARIABLE	INPUT VALUE	COMMENTS
Application Rate (lbs ai/A)	1.0	Proposed maximum use rate in label.

Maximum No. of Applications	1	Proposed maximum number of applications in label.
Application Interval (days)	N/A	Single Application
K_{oc}	350	Application in soil with low adsorption potential, MRID # 42347801
Aerobic Soil Metabolic Half-life (days)	21	MRID # 415733-11. Although the maximum aerobic soil metabolism half life have been reported in one study as 51.3 days, no significant difference in model output was observed by using this rare maximum half life.
Is the pesticide wetted-in?	Yes	Proposed use information in label.
Depth of Incorporation (in.)	0	Proposed use information in label.
Spray Drift (%)	1	Ground application; Aerial or airblast = 5%; Ground = 1%; Granular = 0%. Over 90% application of this chemical uses ground spray.
Solubility (mg/L)	0.8	Solubility at 22 ^{o}C from Pesticide Manual, British Crop Protection Council, 1983.
Aerobic Aquatic Metabolic Half-life (days)	42	21-day aerobic soil metabolism half-life multiplied by 2 to account for a change in media. This is standard guidance in surface water modeling (GENEEC and PRZM-EXAMS) when no acceptable aerobic aquatic metabolism data are available and the compound is stable to hydrolysis.
Photolysis Half-life (days)	22 days	MRID# 41573307

The EEC'S have been calculated so that in any given year, there is a 10% probability that the maximum average concentration of that duration in that year will equal or exceed the EEC at the site. The modeling results are also considered to be conservative and only about an order of magnitude higher than the concentrations reported in the monitoring data from STORET.

Ground Water Inputs (Table 5)

Method for Estimating Concentrations in Ground Water

Results from the SCI-GROW2 (Screening Concentrations in Ground Water) model predict that the maximum chronic concentration of parent diclofop methyl in shallow ground water is not expected to exceed 0.07μg/l for the proposed application of 1 application at 1 lb ai/A/application to Wheat/Barley. In addition to the model, a prospective groundwater study was also conducted by the registrant for diclofop methyl. The final report of the prospective ground water study indicated in the result of findings that at DAT 48 (Days After Treatment) bromide tracers were detected in the shallow ground water wells indicating recharge of aquifer, but no diclofop methyl or its acid metabolites were detected in the groundwater or soil water samples. EFED notes that the predicted concentration in ground water is below the limit of quantitation (1 μg/l) of the prospective ground water study. Therefore, EFED cannot predict with certainty whether they will reach ground water. However, based on the environmental fate properties, and the prospective ground water study, diclofop methyl or its acid metabolite is not expected to reach ground water.

The SCI-GROW2 model is a model for estimating maximum concentrations of pesticides in ground water. SCI-GROW2 provides a screening concentration, an estimate of likely ground water concentrations if the pesticide is used at the maximum allowed label rate in areas with ground water exceptionally vulnerable to contamination. In most cases, a majority of the use area will have ground water that is less vulnerable to contamination than the areas used to derive the SCI-GROW2 estimate.

The SCI-GROW2 model is based on scaled ground water concentration from ground water monitoring studies, environmental fate properties (aerobic soil half-lives and organic carbon partitioning coefficients-K_{oc}'s) and application rates. The model is based on permeable soils that are vulnerable to leaching and on shallow ground water (10-30 feet).

Table 5. Ground Water Exposure Inputs for SCI-GROW2 for Parent Diclofop methyl.

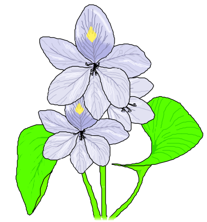
MODEL INPUT VARIABLE	INPUT VALUE	COMMENTS
Application Rate (lbs. ai/A)	1	Proposed maximum use rate in label.
Maximum No. of Applications	1	Proposed maximum number of applications in label.
K_{oc}	350	Application in soil with low adsorption potential, MRID # 42347801
Aerobic Soil Metabolic Half-life (days)	21	MRID # 415733-11.

<u>Monitoring Data</u>

Some monitoring data were available in STORET for diclofop methyl. All of the data reported in the STORET database were from Idaho and Minnesota. Reported concentrations of diclofop methyl in the monitoring data were all below 0.1 ppb (μg/l). All of the reported monitoring data from STORET is attached at the end of this memo. In a Canadian study (Waite, D.T. et al., '92) the movement of several pesticides, including diclofop methyl was observed from 1985 to 1987 in a small, agricultural watershed. Occurrence of diclofop methyl in surface water (pond) samples ranged between 0.05 to 0.47 ppb, and in ground water the maximum detected concentration was 4.88 ppb. There were 37 detections in the Canadian study out of 105 samples in this Canadian ground water study which ranged from a mean of 0.17 to 1.61 ppb. Because of the difference in soil, climatic, and other conditions related to the application of Diclofop, these values are not applicable to the present assessment.

References:

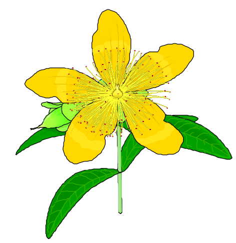
1. Waite, D,T., Grover, R., Westcott, N.D., Sommerstad, H., and Kerr, L. "*Pesticides in Ground Water, Surface water and Spring Runoff in a Small Saskatchewan Watershed*", Environmental Toxicology and Chemistry, Vol. 11, pp. 741-748, 1992.

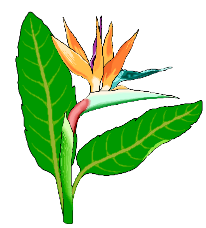


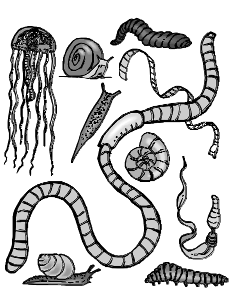
VI   Diclofop Methyl - Ecological Assessment

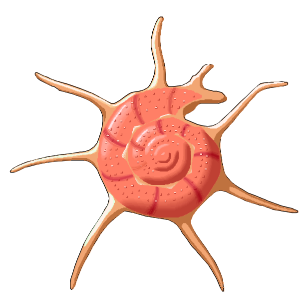
EXECUTIVE SUMMARY

Diclofop methyl is practically nontoxic to birds on an acute basis and poses minimal acute risk. Chronic toxicity to birds is uncertain because tests were not conducted at high enough concentrations, but based on the available information, chronic risk to birds is not likely to be serious. Diclofop methyl is moderately toxic to mammals on an acute basis. It does not pose a high acute risk to mammals except in the case of repeated spot applications to turf. Diclofop methyl poses a potential chronic risk to mammals. Both the acute and chronic risks are enough to trigger concern for risk to threatened and endangered species of mammals. Diclofop methyl is highly toxic on an acute basis to freshwater fish and invertebrates. The primary degradation product, diclofop acid, is only slightly toxic to freshwater fish. Supplemental information also suggest that diclofop methyl is highly toxic to the eastern oyster. In a fish life-cycle test, diclofop methyl affected larval growth at 15 ppb (NOAEC=7.5 ppb). In a waterflea life-cycle test, diclofop methyl affected reproduction at 166 ppb (NOAEC=64 ppb). However, because the environmental fate characteristics of diclofop methyl do not favor transport to surface water, expected environmental concentrations are not expected to reach toxic levels. Thus, acute and chronic risk is minimal to freshwater fish and invertebrates. Diclofop methyl is toxic to terrestrial plants, especially monocots (grasses and sedges). Spray drift and runoff poses a high risk to nontarget terrestrial plants. High risk must also be assumed for nontarget aquatic plants since no toxicity data have been provided on these species.









1. **Ecological Toxicity Data**

a. Toxicity to Terrestrial Animals

i. Birds, Acute and Subacute

Table 1-eco gives results for the acute oral toxicity testing with an upland game bird using technical grade diclofop-methyl. Since the LD_{50} obtained in both studies exceeds 2000 mg/kg, diclofop-methyl is categorized practically nontoxic to avian species on an acute oral basis. The guideline requirement for this test (71-1) is fulfilled by MRID 40072903.

Table 1-eco. Acute Oral Toxicity to birds.

Species	% ai	LD_{50} (mg/kg)	Toxicity Category	MRID No. Author/Year	Study Classification[1]
Northern bobwhite quail *(Colinus virginianus)*	94.5	>2250	Practically nontoxic	40072903 Hinken *et al.*, 1986	Core
Northern bobwhite quail *(Colinus virginianus)*	95	4,400	Practically nontoxic	Acc. No. 097117 1977	Supplemental

[1] "Core" indicates the study satisfies the guideline; "supplemental" indicates the study is scientifically sound, but does not satisfy the guideline.

Table 2-eco gives the results of subacute dietary testing with an upland game bird (the northern bobwhite) and a waterfowl (the mallard) using technical grade diclofop-methyl. Since all of the LC_{50}'s exceed 5000 ppm, diclofop-methyl is categorized as practically nontoxic to birds on a subacute dietary basis. The test guideline requirement (71-2) is fulfilled by MRID 40072901 and 40072902, and Acc. No. 097291.

Table 2-eco. Subacute dietary toxicity to birds.

Species	% ai	5-Day LC_{50} (ppm)[1]	Toxicity Category	MRID No. Author/Year	Study Classification
Northern bobwhite *(Colinus virginianus)*	95	13,000	Practically nontoxic	Acc. No. 097117 Roberts,1977	Core
Northern bobwhite *(Colinus virginianus)*	94.5	>5620	Practically nontoxic	40072901 Hinken *et al.*, 1986	Core
Mallard *(Anas platyrhynchos)*	95	>20,000	Practically nontoxic	Acc. No. 097291	Core
Mallard (*Anas platyrhynchos*)	94.5	>5620	Practically nontoxic	40072902 Hinken *et al.*, 1986	Core
Coturnix quail (*Coturnix coturnix japonica*)	95	>20,000	Practically nontoxic	Acc. No. 094682 Terrell & Parke, 1975	Supplemental

[1] Test organisms observed an additional three days while on untreated feed.

ii. Birds, Chronic

Table 3-eco give results of avian reproductive studies with technical grade active ingredient. The studies found no significant effect of reproduction or parental toxicity at dietary

concentrations up to 200 ppm. The studies are supplemental because the test levels were not high enough to determine the NOAEL and LOAEL, and the highest test concentration was less than the maximum expected environmental concentration (EEC). With a maximum application rate of 1 lb AI/A, the maximum EEC is 240 ppm. Because the available data is sufficient to conclude a low risk of chronic effects to birds, a request to waiver new avian reproduction studies to fulfill this guideline has been approved by EFED (Bar Code #D261423).

Table 3-eco. Avian reproduction toxicity

Species/ Study Duration	% ai	NOAEL (ppm)	LOAEL (ppm)	LOAEL Endpoints	MRID No. Author/Year	Study Classification
Northern bobwhite *(Colinus virginianus)*	94.5	200	Not determined	None	Acc. No. 098297 and 243472	Supplemental
Mallard *(Anas platyrhynchos)*	94.5	200	Not determined	None	Acc. No. 098297 and 243472	Supplemental

iii. Mammals, Acute and Chronic

Wild mammal testing is not required for diclofop methyl because rat toxicity test submitted to the Agency's Health Effects Division (HED) provide adequate information on toxicity to mammals. Table 4-eco gives acute rat toxicity values for technical diclofop methyl and a formulated product. The geometric mean of the LD_{50} for male and female rats is 568 mg ai/kg. This indicates that diclofop-methyl is moderately toxic to small mammals on an acute oral basis.

Table 4-eco. Acute Toxicity to Mammals

Species	% ai	Test type	LD_{50} (mg/kg)	MRID/Acc. No.
Rat (*Rattus norvegicus*)	"Technical"	Acute oral	580 (male) 557 (female)	097107
Rat (*Rattus norvegicus*)	36%	Acute oral	2029 (male) (730 mg ai/kg)	
Rat (*Rattus norvegicus*)	"Technical"	Acute dermal	> 5000	

A limited amount of information on the subchronic toxicity of diclofop acid, the primary degradation product of diclofop methyl, is provided by a subchronic study with the rat (MRID not listed). This study found that a dietary concentration of 500 ppm of diclofop acid caused increased kidney weight in males. The NOAEL was 100 ppm. For comparison, a 30-day feeding study with the rat testing diclofop methyl found increased organ weights in males at a dietary concentration of 80 ppm. This study did not determine the NOAEL. These results indicate that diclofop acid is less toxic to mammals than is the parent compound, diclofop methyl.

Table 5-eco gives the results of some chronic and subchronic mammalian studies that are pertinent to ecological effects. Based on these results, the NOAEL and LOAEL for ecologically significant effects in mammals are established at 30 ppm and 100 ppm, respectively, based on pup mortality observed in the 3-generation reproduction test. It is noteworthy that a short-term (15-week) developmental study showed fetotoxic effects with an oral dose of 32 mg/kg body weight, which is approximately equivalent to an dietary dose of 640 ppm. This indicates that short-term

exposure to diclofop-methyl can impair reproduction of mammals, although somewhat higher doses are required than for long-term exposures.

Table 5-eco. Subchronic and Chronic Toxicity to Mammals

Species	% ai	Test Type	Toxicity Value	Affected Endpoints	MRID/Acc. No.
Rat (*Rattus norvegicus*)	98	3 generation reproduction	NOAEL=30 ppm LOAEL=100 ppm	Increased pup mortality	097111
Rat (*Rattus norvegicus*)	"Tech."	Developmental	Teratogenicity: NOAEL>100 mg/kg (2000 ppm)	Teratogenic: none	097108
			Fetotoxic: NOAEL=10 mg/kg (200 ppm) LOAEL=32 mg/kg (640 ppm)	Fetotoxic: reduced body weight gain, increased resorptions, dilation of renal pelvis, distention of uterus.	
			Maternal: NOAEL<10 mg/kg (200 ppm)	Maternal: increased liver weight	

iv. Insects

A honey bee acute toxicity study (Guideline No. 141-1) is not required for diclofop-methyl because its use sites (wheat, barley, and turf) will not result in much exposure to honey bees.

b. Toxicity to Freshwater Aquatic Animals

i. Freshwater Fish, Acute

Table 6-eco gives the result of acute toxicity testing with freshwater fish using technical grade diclofop methyl and a formulated product. The LC_{50} values for both a coldwater test species (the rainbow trout) and a warmwater test species (the bluegill sunfish) falls in the range of 0.1 to 1 ppm, classifying diclofop-methyl as highly toxic to freshwater fish on an acute basis. The test guideline requirement (72-1) is fulfilled by MRIDs 41573302 and 41606301, and Acc. No. 098297 for the TGAI (72-1(a) and 72-1(c)) and by MRIDs 41606302 and 41606303 for the formulated product.

Table 6-eco. Acute toxicity to freshwater fish

Species, Study type	% AI	96-hour LC_{50} (ppm)	Toxicity Category	MRID No. Author/Year	Study Classification
Rainbow trout *(Oncorhynchus mykiss)* static	95.1	0.23	Highly toxic	41573302 Frank *et al.*, 1990	Core
Rainbow trout *(Oncorhynchus mykiss)*	“Technical”	0.54	Highly toxic	USEPA, 1979	Core
Rainbow trout *(Oncorhynchus mykiss),* static	95	0.25	Highly toxic	USFWS, 1978	Core
Rainbow trout *(Oncorhynchus mykiss)*	95	0.17	Highly toxic	Acc. No. 094682 Reinert & Roger, 1975	Supplemental
Rainbow trout *(Oncorhynchus mykiss)*	“Technical”	0.32	Highly toxic	Acc. No. 098297	Core
Rainbow trout *(Oncorhynchus mykiss),* static	34.8 (3 EC)	0.65 (formulation) 0.22 (AI)	Highly toxic	41606303 Smith & Schweitzer, 1990	Core
Bluegill sunfish *(Lepomis macrochirus)*	95.1	0.15	Highly toxic	41606301 Smith & Schweitzer, 1990	Core
Bluegill sunfish *(Lepomis macrochirus)*	Technical	0.31	Highly toxic	USEPA, 1979	Core
Bluegill sunfish *(Lepomis macrochirus)*	95	0.54	Highly toxic	USFWS, 1978	Core
Bluegill sunfish *(Lepomis macrochirus)*	95	0.29	Highly toxic	Acc. No. 094682 Reinert & Roger, 1975	Supplemental
Bluegill sunfish *(Lepomis macrochirus)*	Technical	0.24	Highly toxic	098297	Supplemental
Bluegill sunfish *(Lepomis macrochirus)*	34.8 (3 EC)	0.36 (formulation) 0.13 (AI)	Highly toxic	41606302 Smith & Schweitzer, 1990	Core

For use in risk assessment, the means of the LC_{50} values from all core studies with the TGAI were determined. These means were 0.34 ppm for the rainbow trout and 0.33 ppm for the bluegill sunfish. According to EFED policy, the risk assessment will be based on the lowest LC_{50} value from a core study, which is 0.15 ppm.

A study with the rainbow trout provides information on the free acid metabolite of diclofop-methyl. The 96-hr LC_{50} was determined to be 21.9 ppm. This indicates that the acid metabolite of diclofop-methyl is less toxic to fish than the parent by almost two orders of magnitude (Acc. No. 098297).

ii. Freshwater Fish, Chronic

Table 7-eco gives results of chronic toxicity testing with freshwater fish using technical grade diclofop-methyl. The results of two early life-stage toxicity tests indicate that concentrations of 46 ppb or greater are detrimental to the survival of immature fish. The life-cycle toxicity test indicates that exposure throughout a fish’s life-cycle will impairment of larval growth at concentrations of 15 ppb or greater. The NOAEC for the most sensitive chronic

endpoint was established at 7.5 ppb. The test guideline requirement for early life-stage testing (72-4) has been fulfilled by MRID 00076867 and Acc. No. 246021, and that for life-cycle testing (72-5) has been fulfilled by MRID 43284601.

Table 7-eco. Chronic toxicity to freshwater fish

Species, Study duration	% ai	NOAEC (ppb)	LOAEC (ppb)	MATC[1] (ppb)	Endpoints Affected	MRID No. Author/Year	Study Classification
Early Life-Stage Toxicity Test							
Fathead minnow (*Pimephales promelas*)	93	39	86	58	Survival, percent hatch	MRID 00076867 Wilson, 1981	Core
Rainbow trout *(Oncorhynchus mykiss)*, 30 days	93	22	46	32	Survival	Acc. No. 246021 Wilson, 1981	Core
Life-Cycle Toxicity Test							
Fathead minnow *(Pimephales promelas)*	95.3	7.5	15	10.6	larval growth	43284601 Dionne, 1994	Core

[1] defined as the geometric mean of the NOAEC and LOAEC.

iii. Freshwater Invertebrates, Acute

Table 8-eco gives the result of acute toxicity testing with freshwater invertebrates using technical grade diclofop methyl and a formulated product. The mean LC_{50} value of the two core studies with the TGAI is 0.39 ppm. The LC_{50} obtained from a test with a formulated product was similar (0.37 ppm AI). Because the LC50's fall within the range of 0.1 to 1 ppm, diclofop-methyl is classified as highly toxic to freshwater fish on an acute basis. The test guideline requirement for the TGAI (72-2(a)) is fulfilled by 41573303 and USEPA (1979), and the test guideline requirement for a TEP (72-2(b)) is fulfilled by 4141606304.

Table 8-eco. Acute toxicity to freshwater invertebrate

Species Static or Flow-through	% AI	48-hour LC_{50}/ EC_{50} (ppm)	Toxicity Category	MRID No. Author/Year	Study Classification
Waterflea *(Daphnia magna)*, static	95.1	0.23	Highly toxic	41573303 Frank *et al.*, 1989	Core
Waterflea *(Daphnia magna)*	“Technical”	0.54	Highly toxic	USEPA, 1979	Core
Waterflea *(Daphnia magna)*, static	34.8	1.06 (formulation) 0.37 (a.i.)	Moderately toxic (formulation), highly toxic (a.i.)	41606304 Smith & Schweitzer, 1990	Core
Waterflea *(Daphnia magna)*	34.8	1.9 (formulation) 0.66 (a.i.)	Moderately toxic (formulation), highly toxic (a.i.)	ESVIIH, 1978	Supplemental

iv. Freshwater Invertebrate, Chronic

Table 9-eco gives the results from a freshwater aquatic invertebrate life-cycle test using technical diclofop methyl. This test found that diclofop methyl caused a reduction in number of eggs produced at a concentration of 166 ppb, whereas a concentration of 64 ppb caused no significant observed effect. The test guideline requirement (72-4) is fulfilled by MRID 41737902.

Table 9-eco. Life-cycle toxicity with a freshwater aquatic invertebrate.

Species, Study type	% ai	21-day NOAEC (ppb)	LOAEC (ppb)	MATC[1] (ppb)	Endpoints Affected	MRID No. Author/Year	Study Classification
Waterflea *(Daphnia magna)*, static renewal	95.1	64	166	103	Number of young produced	41737902 Smith, 1990	Core

[1] defined as the geometric mean of the NOAEC and LOAEC.

c. Toxicity to Estuarine and Marine Animals

i. Estuarine and Marine Fish

Toxicity testing with estuarine/marine fish is not required for current uses of diclofop-methyl (wheat, barley, and turf) because little of these uses occur in coastal areas. The majority of use is on wheat and barley (88.9% of pounds sold), which is grown mostly in inland areas (Fig. 1 and 2). Use on turf is only as a Special Local Need registration for use on golf courses in 11 states and is a minor use of diclofop-methyl (2.6% of pounds sold). Only a small portion of the golf course use is expected to be adjacent to estuarine areas. Furthermore, the risk to estuarine/marine habitats is expected to be minimal because risk quotients for freshwater species are very small, environmental fate properties of the active ingredient does not favor transported into surface or ground water, and exposure to spray drift by aerial applications is mitigated through a requirement of a 100-ft buffer zone. Therefore, the test guideline for acute toxicity to estuarine/marine fish (72-3a) is waived, although it might be required in the future if additional uses are added. Chronic toxicity testing with a marine/estuarine fish is not required.

iii. Estuarine and Marine Invertebrates, Acute

Toxicity testing with estuarine/marine invertebrates is not required for current uses of diclofop-methyl (wheat, barley, and turf) because, as described above, little of these uses occur in coastal areas. Acute oyster toxicity studies have been conducted with diclofop-methyl and the diclofop-methyl metabolite 2-(4-(2,4-dichlorophenoxy) phenoxy) propionic acid (Acc. No. 245123; however, the results of these studies are considered invalid because the percent active ingredient of the test material was not identified. These studies do not need to be repeated at this time, although they might be required in the future if additional uses are added to the label. Chronic toxicity testing with a marine/estuarine invertebrate is not required.

d. Toxicity to Plants

i. Terrestrial

Tier 2 terrestrial plant testing is required for diclofop methyl because it is an herbicide that has terrestrial non-residential outdoor use patterns, could move off the application site via runoff and spray drift (for aerial applications), and might affect endangered or threatened plant species associated with the application sites. The required testing consists of seedling emergence and vegetative vigor tests with ten crop species. Six of the species must be dicotyledonous and represent at least four families. One of these species must be soybean (*Glycine max*) and a second must be a root crop. The remaining four species must be monocotyledonous and represent at least two families. One of these species must be corn (*Zea mays*).

Results of tier 2 seedling emergence testing are given in Table 10-eco. Ryegrass is the most sensitive monocotyledon and the most sensitive species overall, with an EC_{25} of 0.012 lb ai/A and an NOAEC of 0.0063 lb ai/A. Lettuce was the most sensitive dicotyledon. These data indicate that monocotyledons are much more sensitive to diclofop methyl than are dicotyledons. The guideline for seedling emergence testing (123-1a) is fulfilled (MRID 41606306).

Table 10-eco. Seedling emergence toxicity of nontarget terrestrial plant (Tier II)

Species	% ai	EC_{25} (lb ai/A)	NOAEC (lb ai/A)	Most Sensitive Endpoint	MRID No. Author/Year	Study Classification
Corn (monocot)	95.1	0.083	0.100	Radical length	41606306 Chetram, 1990	Core
Oat (monocot)	95.1	0.362	0.125	Plant height	41606306 Chetram, 1990	Core
Onion (monocot)	95.1	0.394	0.500	Plant height	41606306 Chetram, 1990	Core
Ryegrass (monocot)	95.1	0.012	0.0063	Plant height (based on the EC_{25}) or radical length (based on the NOAEC)	41606306 Chetram, 1990	Core
Carrot (dicot, root crop)	95.1	>1.0	1.0	N/A	41606306 Chetram, 1990	Core
Soybean (dicot)	95.1	> 1.0	1.0	N/A	41606306 Chetram, 1990	Core
Cabbage (dicot)	95.1	1.25	0.5	Plant height	41606306 Chetram, 1990	Core
Cucumber (dicot)	95.1	> 1.0	1.0	N/A	41606306 Chetram, 1990	Core
Lettuce (dicot)	95.1	0.792	0.25	Plant dry weight	41606306 Chetram, 1990	Core
Tomato (dicot)	95.1	> 1.0	1.0	N/A	41606306 Chetram, 1990	Core

Results of tier 2 vegetative vigor testing are given in Tables 11-eco. Results were similar to the seedling emergence test in showing that monocotyledons are much more sensitive to diclofop methyl than are dicotyledons. Ryegrass is the most sensitive monocotyledon and the most sensitive species overall, with an EC_{25} of 0.10 lb ai/A and an NOAEC of 0.0625 lb ai/A. Lettuce was the most sensitive dicotyledon. The guideline for vegetative vigor testing (123-1b) is fulfilled (MRID 41606306).

Table 11-eco. Vegetative vigor toxicity to nontarget terrestrial plant (Tier II)

Species	% ai	EC_{25} (lb ai/A)	NOAEC (lb ai/A)	Most Sensitive Endpoint	MRID No. Author/Year	Study Classification
Corn (monocot)	95.1	0.101	0.05	Plant height	41606305 Chetram, 1990	Core
Oat (monocot)	95.1	> 0.5	0.5	N/A	41606305 Chetram, 1990	Core
Onion (monocot)	95.1	> 1.0	1.0	N/A	41606305 Chetram, 1990	Core
Ryegrass (monocot)	95.1	0.10	0.0625	Plant height	41606305 Chetram, 1990	Core
Carrot (dicot, root crop)	95.1	> 1.0	1.0	N/A	41606305 Chetram, 1990	Core
Soybean (dicot)	95.1	>1.0	1.0	N/A	41606305 Chetram, 1990	Core
Cabbage (dicot)	95.1	4.69	0.500	Plant height	41606305 Chetram, 1990	Core
Cucumber (dicot)	95.1	>1.0	1.0	N/A	41606305 Chetram, 1990	Core
Lettuce (dicot)	95.1	1.00	0.50	Plant dry weight	41606305 Chetram, 1990	Core
Tomato (dicot)	95.1	>1.0	1.0	N/A	41606305 Chetram, 1990	Core

Data are not available on the phytotoxicity of diclofop acid, the major degradation product of diclofop methyl.

ii. Aquatic Plants

Aquatic plant testing is required for any herbicide that has outdoor non-residential terrestrial uses that may move off-site by runoff, by drift, or that is applied directly to water. The following species should be tested at Tier I: *Pseudokirchneria subcapitata* and *Lemna gibba*. Aquatic Tier II studies are required for all low dose herbicides (those with the maximum use rate of 0.5 lbs ai/A or less) and any pesticide showing a negative response equal to or greater than 50% in Tier I tests. The following species should be tested at Tier II: *Pseudokirchneria subcapitata*, *Lemna gibba*, *Skeletonema costatum*, *Anabaena flos-aquae*, and a freshwater diatom. No aquatic plant testing has been submitted for diclofop-methyl or diclofop acid. The test guideline requirement (122-2 and 123-2) have not been fulfilled.

3. Exposure and Risk Characterization

Risk characterization integrates exposure and ecotoxicity data to evaluate the likelihood of adverse effects. For ecological effects, the Agency accomplishes this integration using the quotient method. Risk quotients (RQs) are calculated by dividing exposure estimates by acute and chronic ecotoxicity values.

$$RQ = EXPOSURE / TOXICITY$$

RQs are then compared to the Office of Pesticide Programs's levels of concern (LOCs) to assess potential risk to nontarget organisms and the need to consider regulatory action. Calculation of a RQ that exceeds the LOC indicates that a particular pesticide use poses a presumed risk to nontarget organisms. LOCs currently address the following categories of presumed risk: (1) **acute high** -- potential for acute risk is high and regulatory action beyond restricted use classification may be warranted, (2) **acute restricted use** -- the potential for acute risk is high, but may be mitigated through restricted use classification, (3) **acute endangered species** - threatened and endangered species may be adversely affected, and (4) **chronic risk** - the potential for chronic risk is high and regulatory action may be warranted.

The ecotoxicity values used in the acute and chronic risk quotients are endpoints derived from required laboratory toxicity studies. Ecotoxicity endpoints derived from short-term laboratory studies that assess acute effects are: (1) LC_{50} (fish and birds), (2) LD_{50} (birds and mammals), (3) EC_{50} (aquatic plants and aquatic invertebrates) and (4) EC_{25} (terrestrial plants). The ecotoxicity endpoints derived from long-term laboratory studies that is used to assess chronic effects is the NOAEC. Table 12-eco gives formulas for calculating RQ's and gives LOC's for various risk presumptions.

Table 12-eco. Risk Presumptions and Corresponding LOC's and RQ formulas

Risk Presumption	RQ	LOC
	Terrestrial and Aquatic Animals	
Acute High Risk	EEC[1]/LC_{50}	0.5
Acute Restricted Use	EEC/LC_{50}	0.2
Acute Endangered Species	EEC/LC_{50}	0.1
Chronic Risk	EEC/NOAEC	1.0
	Terrestrial and Semi-Aquatic Plants	
Acute High Risk	EEC/EC_{25}	1.0
Acute Endangered Species	EEC/NOAEC or EC_{05}	1.0
	Aquatic Plants	
Acute High Risk	EEC/EC_{50}	1.0
Acute Endangered Species	EEC/NOAEC or EC_{05}	1.0

[1] abbreviation for Estimated Environmental Concentration

a. Exposure and Risk to Nontarget Terrestrial Animals

i. Terrestrial Exposure Assessment

To calculate risk of application of diclofop methyl to terrestrial animals, the estimated environmental concentrations (EECs) on food items following product application were compared to dietary LC_{50} values. The predicted 0-day maximum residues of the pesticide on selected avian or mammalian food items immediately following a direct single application at 1 lb ai/A were derived based on the nomogram of Hoeger and Kenaga (1972), as modified by Fletcher *et al*. (1994) (Table 13-eco).

Table 13-eco. Estimated Environmental Concentrations on Avian and Mammalian Food Items (ppm) Following a Single Application at 1 lb ai/A.

Food Items	EEC (ppm) Predicted Maximum Residue[1]	EEC (ppm) Predicted Mean Residue[1]
Short grass	240	85
Tall grass	110	36
Broadleaf/forage plants and small insects	135	45
Fruits, pods, seeds, and large insects	15	7

[1] Predicted maximum and mean residues are for a 1 lb ai/a application rate and are based on Hoerger and Kenaga (1972) as modified by Fletcher *et al.* (1994).

Diclofop methyl may be applied to turf with repeated applications. For broadcast applications, the maximum rate per year allowed by the label is 1 lb ai/A. Therefore, the assessment of a single application at 1 lb ai/A is protective for multiple broadcast applications on turf as well. For spot treatments, the maximum rate per year allowed by the label is 1.53 lb ai/A. Risk for multiple spot treatments were assessed by assuming a single application at 1 lb ai/A followed by a second application of 0.53 lb ai/A seven days after the first application. Dissipation of residues on wildlife food items between applications was taken into account. Residues were assumed to dissipate following first-order dissipation model. The only foliage dissipation information that is available is a summary of a study conducted by the registrant that has not been submitted to the Agency for a formal review. Therefore, for the current risk assessment, an half-life of 30 days was assumed.[2] Peak residues were calculated by adding residues remaining after 7 days following the first application of 1 lb ai/A to initial residues predicted for an application of 0.53 lb ai/A. These peak residues for spot treatment on turf are: 331 ppm for short grass, 152 ppm for tall grass, 186 ppm for broadleaf plants and small insects, and 21 ppm for seeds.

i. Birds

For all use sites and application methods of diclofop methyl, acute risk quotients for terrestrial organisms are less than 0.1 (Table 14-eco). Since all acute risk quotients are less than

[2] EFED Policy Memorandum of 26 August 1999 states:

> "In the absence of foliar dissipation data, the shortest half-life among hydrolysis, photolysis, or volatilization should be multiplied by three. If the calculation results in a product greater than 30 days, 30 days should be used as the model input for dissipation half-life."

> For diclofop methyl, the half-lives for hydrolysis (pH 7) and photolysis in water were 32 and 22 days, respectively. Diclofop methyl does not volatilize rapidly. Since three times each of these half-lives would be greater than 30 days, a half-life of 30 days was used as a model input.

the LOC for high acute risk (0.5) and risk to endangered species (0.1), all uses of diclofop methyl are predicted to pose minimal risk to birds on an acute basis.

For single broadcast applications on wheat, barley, and turf at 1.0 lb ai/A, chronic avian risk quotients for reproductive effects range from 0.08 (seeds) to 1.2 (short grass). Since the short grass risk quotients exceed the chronic risk LOC of 1, chronic risk is not ruled out. However, avian reproduction studies have shown that diclofop-methyl caused no reproductive effects at 200 ppm, the highest concentration tested. The upper bound of concentrations in short grass, 240 ppm, is only slightly above this level. Furthermore, field residue studies indicate that residues of diclofop methyl and primary degradation products on wheat dissipate very rapidly (half-life 0.42-1.24 days). Therefore, chronic risk to birds might not be high, even for birds eating short grass. See the risk characterization section of this chapter for further discussion.

Multiple spot applications of diclofop methyl may be made on turf. The maximum per season rate for use on turf is 1.53 lb ai/A for spot treatments. The chronic risk quotient for birds feeding on short grass is 1.66, indicating possible chronic risk to birds. Again, it is possible that further testing at higher levels would reveal that the actual NOAEL is above the EEC of 331 ppm. Therefore, the chronic risk conclusion for birds consuming short grass is uncertain, although somewhat more likely than the conclusion of chronic risk for broadcast applications.

Table 14-eco. Acute and chronic risk quotients for birds. Risk quotients are based on an LC_{50} is for the northern bobwhite and an NOAEL for the northern bobwhite and mallard duck.

Use Site; Application Method	Food Items	Maximum EEC (ppm)	LC50 (ppm)	NOAEC (ppm)	Risk Quotient	
					Acute (EEC/LC_{50})	Chronic (EEC/NOAEL)
Wheat, barley, and turf; single broadcast application at 1 lb ai/A	Short grass	240	13,000	200	0.02	1.20 a
	Tall grass	110	13,000	200	0.01	0.55
	Broadleaf plants/Insects	135	13,000	200	0.01	0.68
	Seeds	15	13,000	200	<0.01	0.08
Turf; 2 spot application at 1 and 0.53 lb ai/A, separated by 7 days	Short grass	331	13,000	200	0.03	1.66 a
	Tall Grass	152	13,000	200	0.01	0.76
	Broadleaf plants/Insects	186	13,000	200	0.01	0.93
	Seeds	21	13,000	200	<0.01	0.11

a Exceeds chronic LOC.

ii. Mammals

Estimating the potential for adverse effects to wild mammals is based upon EEB's draft 1995 SOP of mammalian risk assessments and methods used by Hoerger and Kenaga (1972) as modified by Fletcher *et al.* (1994). The concentration of diclofop-methyl in the diet that is expected to be acutely lethal to 50% of the test population (LC50) is determined by dividing the LD50 value (usually rat LD50) by the proportion of body weight consumed per day. A risk quotient is then determined by dividing the EEC by the derived LC_{50}. Risk quotients are calculated for three separate weight classes of mammals (15, 35, and 1000 g), each presumed to consume four different kinds of food (grass, forage, insects, and seeds).

For use of diclofop methyl on wheat, barley, and turf (single broadcast applications at 1.0 lb ai/A), acute risk quotients for mammals are all below the LOC for high risk (0.5), and thus does not pose a high risk to non-endangered mammals (Table 15-eco). However, some risk quotients exceed the LOC for risk that might be mitigated through restricted use classification (0.2) and risk to endangered species (0.1). For spot treatment on turf with repeated applications, the acute risk quotient for small herbivorous mammals feeding on short grass (0.55) exceeds the high acute risk LOC (0.5) (Table 15-eco). This indicates that repeated spot applications of diclofop methyl on turf poses a high acute risk to herbivorous mammals. Risk quotients for other types of mammals were below the LOC for high risk, but exceeded the LOC for risk that might be mitigated through restricted use classification (0.2) and risk to endangered species. The results indicate that only spot treatments with repeated applications pose a high risk to mammals, all uses of diclofop methyl poses enough risk to cause concern for effects on endangered and threatened species of small mammals.

Table 15-eco. a. Acute risk quotients for herbivorous and insectivorous mammals, based on the rat LD50.

Use Site	Body Weight (g)	% Body Weight Consumed	Rat LD50 (mg/kg)	EEC (ppm) Short Grass	EEC (ppm) Forage & Small Insects	EEC (ppm) Large Insects	Acute Risk Quotient[1]		
							Short Grass	Forage & Small Insects	Large Insects
Wheat, barley, and turf; single broadcast application at 1 lb ai/A	15	95	568	240	135	15	0.40**	0.23**	0.03
	35	66	568	240	135	15	0.28**	0.16*	0.02
	1000	15	568	240	135	15	0.06	0.04	<0.01
Turf; 2 spot application at 1 and 0.53 lb ai/A, separated by 7 days	15	95	568	331	186	21	0.55***	0.31**	0.04
	35	66	568	331	186	21	0.38**	0.22**	0.02
	1000	15	568	331	186	21	0.09	0.05	<0.01

[1] RQ = EEC (ppm) x Proportion Body Weight Consumed / LD50 (mg/kg)

* Exceeds LOC for risk to threatened and endangered species.
** Exceeds LOC for risk that may be mitigated through restricted use registration.
*** Exceeds LOC for high acute risk.

Table 15-eco. b. Acute risk quotients for granivorous mammals, based on the rat LD50 .

Application Site	Body Weight (g)	% Body Weight Consumed	Rat LD50 (mg/kg)	EEC (ppm) Seeds	Acute RQ[1] Seeds
Wheat, barley, and turf; single broadcast application at 1 lb ai/A	15	21	568	15	<0.01
	35	15	568	15	<0.01
	1000	3	568	15	<0.01
Turf; 2 spot application at 1 and 0.53 lb ai/A, separated by 7 days	15	21	568	21	<0.01
	35	15	568	21	<0.01
	1000	3	568	21	<0.01

[1] RQ = EEC (ppm) x Proportion Body Weight Consumed / LD50 (mg/kg)

As a screen for chronic risk, risk quotients were calculated by dividing the maximum initial EEC, based on the method of Fletcher *et al.* (1994), divided by the NOAEL obtained in a chronic rat study. The NOAEL of 30 ppm was chosen for use in ecological risk assessment based on increased pup mortality in a 3-generational reproduction study (NOAEL 30 ppm) and fetotoxic effects observed in a developmental toxicity study (NOAEL=32 ppm). Chronic risk quotients for mammals range from 0.50 to 8.0 (Table 16-eco). Because risk quotients for all food types except seeds exceed the chronic LOC (1.0), all uses of diclofop-methyl may pose a chronic risk to mammals and may harm threatened and endangered mammal species.

Table 16-eco. Chronic Risk Quotients for mammals for diclofop methyl, based on a rat results of 15-day developmental test and a 3-generation reproduction test.

Application Site	Food Items	Maximum EEC (ppm)	NOAEL[1] (ppm)	Chronic RQ (EEC/NOAEC)
Wheat, barley, and turf; single broadcast application at 1 lb ai/A	Short grass	240	30	8.00
	Tall grass	110	30	3.67
	Broadleaf plants/Insects	135	30	4.50
	Seeds	15	30	0.50
Turf; 2 spot application at 1 and 0.53 lb ai/A, separated by 7 days	Short grass	331	30	11.0
	Tall grass	152	30	5.07
	Broadleaf plants/Insects	186	30	6.20
	Seeds	21	30	0.70

1 The NOAEL of 30 ppm is from the a rat 3-generation reproduction test, but is essentially identical to the NOAEL of 32 ppm obtained in a 15-day rat developmental test. Therefore, an exposure duration does not seem to be necessary to induce chronic effects in mammals.

Since the risk screen indicates that there may be a chronic risk, risk could be further evaluated by comparing the estimated EEC's over time with the chronic mammal LOAEL and NOAEL. This analysis is dependent on accurate estimation of the half-life of diclofop methyl on foliage. Based on submitted laboratory data on degradation rates, EFED would assume an half-life of 30 days.[3] However, unreviewed data submitted by Hoechst Celanese Corporation indicate

[3] See preceding footnote in the Terrestrial Exposure section.

a much shorter half-life of 0.42-1.25 days. Because of this very high level of uncertainty, the analysis of EEC's over time was not performed. Submittal of the complete study reports of the field residue studies yielding the short half-life values would allow the Agency to better assess the chronic risk to mammals.

iii. Insects

The currently registered uses of diclofop methyl are not associated with much exposure to honey bees. Therefore, no data have been required for toxicity to bees, and no label precautionary statement is required.

b. Exposure and Risk to Nontarget Freshwater Aquatic Animals

As a tier 1 screen, EFED calculates EECs using the Generic Expected Environmental Concentration Program (GENEEC). Since use of these EEC's in the aquatic risk assessment indicated risk to some organisms, the EEC's were refined using the PRZM and EXAMS models (Table 17-eco). The Pesticide Root Zone Model (PRZM2) simulates pesticides in field runoff. The Exposure Analysis Modeling System (EXAMS II) simulates pesticide fate and transport in an aquatic environment (one hectare body of water, two meters deep). Refined EECs were calculated only for use of diclofop methyl on wheat and barley in southern states. As evident in the GENEEC results, the soil and weather characteristics associated with this site makes it the worst case scenario, making it protective of aquatic organisms for all uses. Since the risk assessment based on this worst case scenario leads to the conclusion of low risk to aquatic organisms, low risk also can be assumed for use on turf and wheat/barley in northern states.

Table 17-eco. Estimated Environmental Concentrations (EECs) for Aquatic Exposure

Application Site	Application Method	Application Rate (lbs ai/A)	Number of Applications	Initial (Peak) EEC (ppb)	21-day average EEC (ppb)	56-day average EEC(ppb)
Wheat/Barley (Southern)	Ground spray	1	1	1.47	1.11	0.773

ii. Fish and Aquatic Invertebrates

Acute and chronic risk quotients for fish and aquatic invertebrates are given in Table 18-eco. No risk quotient exceeds the LOC for high risk or risk to threatened or endangered species. These risk quotients were calculated based on refined EECs for use on wheat and barley. As EEC's for use on turf (excluding spot treatments) would be lower, the conclusion of low risk applies to broadcast treatments on turf as well. Data were not available to assess the risk to marine/estuarine fish or invertebrates.

Table 18-eco. Acute and chronic risk quotients for fish and aquatic invertebrates from a single application of diclofop-methyl on wheat, barley, or turf.

Type of Organism	Test Species	LC_{50} (ppb)	NOAEC (ppb)	EEC (ppb)		Risk Quotient	
				Initial	Chronic	Acute (EEC/LC_{50})	Chronic (EEC/NOAEC)
Freshwater fish	Bluegill sunfish (acute) and fathead minnow (chronic)	150	7.5	1.47	0.77	0.01	0.10
Freshwater Invertebrates	Waterflea (*Daphnia magna*)	390	64	1.47	1.11	<0.01	0.02

* Exceeds the LOC for risk to threatened and endangered species

Diclofop-methyl may be applied with repeated applications on turf. The maximum application rate per year is 1 lb ai/A for general broadcast applications, but 1.53 lb ai/A for spot applications. Therefore, EEC's for spot applications theoretically could be greater than those estimated using GENEEC for a single application at 1 lb ai/A. In actuality, it is unlikely that EEC's for spot treatment would exceed those for broadcast applications because spot treatment would likely involve treatment of a much smaller percentage of the watershed, leading to less contamination to water from spray drift and runoff. Also, degradation and dissipation of residues taking place between repeated applications would reduce the maximum EEC. Nevertheless, one could conduct a risk screen by assuming that multiple applications from spot treatments on turf would result in EEC's (at most) 1.53 times greater than that for a single application at 1 lb ai/A, thereby increasing the risk quotients by 1.53. Increasing the risk quotients in Table 19-eco by 1.53 would result in values that are still below all of the acute and chronic LOC's. Therefore, we conclude that repeated spot applications on turf would pose minimal acute and chronic risk to aquatic organisms.

d. Exposure and Risk to Nontarget Plants

i. Dry and Semi-aquatic Areas

The EFED does separate risk assessments for two categories of nontarget plants, terrestrial and semi-aquatic. Non-target terrestrial plants inhabit non-aquatic areas which are generally well drained. Non-target semi-aquatic plants inhabit low-lying areas that are usually wet, although they may be dry during certain times of the year. Both the terrestrial and semi-aquatic plants are exposed to pesticides from runoff, drift, and volatilization. They differ, however, in that terrestrial plants are assumed to be subjected to sheet runoff, whereas semi-aquatic plants are assumed to be subjected to channelized runoff.

The EFED assumes that runoff will expose nontarget plants to a fixed percentage of the application rate. This percentage is estimated based on the water solubility of the active ingredient:

Water Solubility	% Runoff Assumed
< 10 ppm	1%
10 - 100 ppm	2%

> 100 ppm	5%

Since the water solubility of diclofop methyl at 20°C is 0.8 ppm, the percent runoff is assumed to be 1%. This assumed runoff value is confirmed by Cessna et al. (1996), who found that approximately 1% of an application of diclofop was lost in runoff from a wheat field following four irrigations. For non-target terrestrial plants, EFED assumes a scenario in which plants are exposed from sheet runoff. A treated site of 1 acre is assumed to drain into an adjacent area of 1 acre where terrestrial plants may be impacted. In the scenario used for non-target semi-aquatic plants, exposure from runoff is assumed to be from channelized runoff. A treated site of 10 acres is assumed to drain into a distant low-lying area of 1 acre where semi-aquatic plants may be impacted.

Exposure from spray drift was assumed to be 1% and 5% of the application rate for ground and aerial applications, respectively. Exposure from spray drift is compared to toxicity observed in the vegetative vigor test to assess risk from foliage exposure. Spray drift exposure is also added to runoff exposure, and the total loading to soil in nontarget areas is compared to toxicity results of the seedling emergence test to assess risk from soil exposure. Table 19-eco gives estimated exposure values for spray drift and total loading to nontarget soils.

Table 19-eco. Estimated exposure (lbs ai/A) in nontarget areas from drift and runoff resulting from a single application of diclofop methyl at 1 lb ai/A.

Application Method	Maximum Application Rate (lb ai/A)	Sheet Run-off (lbs ai/A)	Channelized Runoff (lbs ai/A)	Drift (lbs ai/A)	Total Loading	
					Adjacent Area (Sheet Run-off+Drift)	Semi-aquatic Area (Channel Run-off+Drift)
Aerial	1	0.006	0.06	0.05	0.056	0.11
Ground	1	0.01	0.10	0.01	0.02	0.11

Risk quotients for nontarget terrestrial plants are given in Table 20-eco. **Since risk quotients exceed the LOC of 1, use on diclofop methyl on wheat, barley, and turf is predicted to pose high risk to nontarget terrestrial plants. Threatened and endangered species would be at risk if they are exposed to runoff and spray drift.** Risk stems from effects on seedling emergence and growth from soil exposure. Effects on vegetative vigor from spray drift alone are predicted to be minor.

Table 20-eco. Acute risk quotients for nontarget terrestrial plants, based on seedling emergence and vegetative vigor toxicity to ryegrass.

Method of Application	Seedling Emergence Toxicity (lbs ai/A)	Vegetative Vigor Toxicity (lbs ai/A)	Drift (lbs ai/A)	Total Loading		Risk Quotient		
				Dry Area (Sheet Runoff+ Drift)	Semi-aquatic Area (Channelized Runoff+ Drift)	Emergence		Vegetative Vigor
						Dry Area	Semi-aquatic Area	All Areas
Nonendangered Species								
Aerial	0.012 (EC_{25})	0.10 (EC_{25})	0.05	0.056	0.11	4.67	9.17	0.50

Table 20-eco. Acute risk quotients for nontarget terrestrial plants, based on seedling emergence and vegetative vigor toxicity to ryegrass.

Method of Application	Seedling Emergence Toxicity (lbs ai/A)	Vegetative Vigor Toxicity (lbs ai/A)	Drift (lbs ai/A)	Total Loading		Risk Quotient		
				Dry Area (Sheet Runoff+ Drift)	Semi-aquatic Area (Channelized Runoff+ Drift)	Emergence: Dry Area	Emergence: Semi-aquatic Area	Vegetative Vigor: All Areas
Ground	0.012	0.10	0.01	0.02	0.11	1.66	9.17	0.10
Endangered Species								
Aerial	0.0063 (NOAEL)	0.0625 (NOAEL)	0.05	0.056	0.11	8.89	17.46	0.80
Ground	0.0063	0.0625	0.01	0.02	0.11	3.17	17.46	0.16

Diclofop methyl may rapidly transform in the environment into diclofop acid, especially under alkaline conditions. The phytotoxicity of diclofop acid is unknown.

ii. Aquatic Plants

Exposure to nontarget aquatic plants may occur through runoff and spray drift from treated sites. An aquatic plant risk assessment for acute high risk is usually made for aquatic vascular plants based on toxicity to duckweed (*Lemna gibba*). Non-vascular aquatic plant risk assessments are performed using the most sensitive of four test species of algae and diatoms. An aquatic plant risk assessment could not be conducted for diclofop methyl or diclofop acid because no aquatic plant toxicity data have been submitted. Without toxicity data, high risk to aquatic plants must be assumed.

4. Endangered Species

Levels of concern are exceeded for endangered and threatened species of birds, mammals, and terrestrial plants. Risk to aquatic plants is also assumed. Risk to threatened and endangered species of birds due to possible chronic effects, which are uncertain without additional data.

The Agency has developed a program (the "Endangered Species Protection Program") to identify pesticides whose use may cause adverse impacts on endangered and threatened species, and to implement mitigation measures that will eliminate the adverse impacts. At present, the program is being implemented on an interim basis as described in a Federal Register notice (54 FR 27984-28008, July 3, 1989), and is providing information to pesticide users to help them protect these species on a voluntary basis. As currently planned, the final program will call for label modifications referring to required limitations on pesticide uses, typically as depicted in county-specific bulletins or by other site-specific mechanisms as specified by state partners. A final program, which may be altered from the interim program, will be described in a future Federal Register notice. The Agency is not imposing label modifications at this time through the RED. Rather, any requirements for product use modifications will occur in the future under the Endangered Species Protection Program.

5. Labeling Requirements

a. Manufacturing-Use Products

For registered end-use products, technical products and other manufacturing use products, i.e. those used to formulate other products, a "point source discharge" is a possibility - where effluent from the manufacturing plant may contain pesticides. The following National Pollutant Discharge Elimination System (NPDES) statement (as outlined in Pesticide Regulation (PR) Notice 93-10 (Reference: PR-93-10)) is required:

> "Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System (NDPES) permit and the permitting authority has been notified in writing prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact your State Water Board or Regional Office of the EPA."

b. End-use Products

All products with directions for outdoor terrestrial uses must have the following statements in the Environmental Hazards section:

> “Do not apply directly to water, or to areas where surface water is present or to intertidal areas below the mean high water mark. Do not contaminate water when disposing of equipment washwaters or rinsate."

Labels for products that may be applied via aerial applications (wheat and barley uses) should retain the following statement requiring a 100-ft buffer zone:

> “DO NOT make aerial applications within 100 feet of a lake, stream, drainage basin, tidal marsh, or estuary.”

References

Cessna, A.J., Elliott, J.A., Best, K.B., Grover, R., and Nicholaichuk. 1996. Transport of nutrients and postemergence applied herbicides in runoff from corrugation irrigation of wheat. *In* Herbicide metabolites in surface water and groundwater. pp. 151-164. American Chemical Society.

Appendix E

EEC Formulas for Plant EECs

1. Calculating EECs for terrestrial plants inhabiting dry areas adjacent to treatment sites

Unincorporated ground application:
Runoff = maximum application rate (lbs ai/A) x runoff value
Drift = maximum application rate x 0.01
Total Loading = runoff (lbs ai/Acre) + drift (lbs ai/A)

Incorporated ground application:
Runoff = [maximum application rate (lbs ai/A) ÷ minimum incorporation depth (cm.)] x
runoff value
Drift = maximum application rate x 0.01
(Note: drift is not calculated if the product is incorporated at the time of application.)
Total Loading = runoff (lbs ai/A) + drift (lbs ai/A)

Aerial, airblast, forced-air, and chemigation applications:
Runoff = maximum application rate (lbs ai/A) x
0.6 (60% application efficiency assumed) x
runoff value
Drift = maximum application rate (lbs ai/A) x 0.05
Total Loading = runoff (lbs ai/A) + drift (lbs ai/A)

2. Calculating EECs for terrestrial plants inhabiting semi-aquatic low-lying areas

Unincorporated ground application:
Runoff = maximum application rate (lbs ai/A) x runoff value x 10 acres
Drift = maximum application rate x 0.01
Total Loading = runoff (lbs ai/A) + drift (lbs ai/A)

Incorporated ground application:
Runoff = [maximum application rate (lbs ai/A)/minimum incorporation depth (cm)] x
runoff value x 10 acres
Drift = maximum application rate x 0.01
(Note: drift is not calculated if the product is incorporated at the time of application.)
Total Loading = runoff (lbs ai/A) + drift (lbs ai/A)

Aerial, airblast, and forced-air applications:
Runoff = maximum application rate (lbs ai/Acre) x
0.6 (60% application efficiency assumed) x
runoff value x 10 acres
Drift = maximum application rate (lbs ai/A) x 0.05
Total Loading = runoff (lbs ai/A) + drift (lbs ai/A)